METHOD AND APPARATUS FOR MEASURING RESIDUAL CHLORINE, AND PROBE FOR DETECTING RESIDUAL CHLORINE

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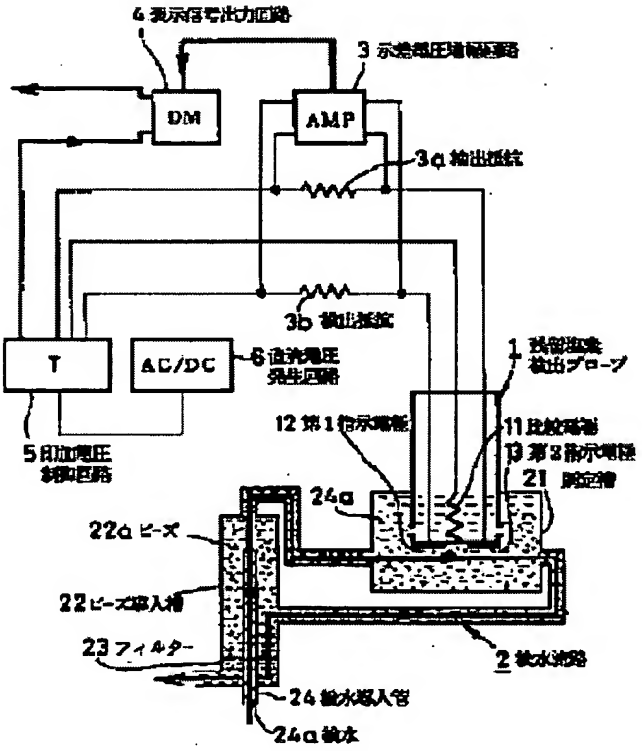
Abstract of **JP10082761**

PROBLEM TO BE SOLVED: To provide a method and apparatus by which even an extremely small amount of residual chlorine can be correctly measured without need for a complicated operation such as calibration using a calibration liquid and without a danger of an error caused by residual current or the like. SOLUTION: Two, first and second indicator electrodes 12, 13 are provided as indicator electrodes whose oxidation-reduction potential varies depending on a residual chlorine amount contained in sample water 24a when in contact with the sample water 24a. In this case, different voltage from one another is applied respectively to each of the first and second indicator electrodes 12, 13 and a circuit including a reference electrode 11, and polaro-current in each circuit is sensed, and the difference is taken thereby offsetting residual current or the like. Thus a complicated calibration operation or the like using calibration liquid is eliminated, so that correct measurement is immediately possible.



CLAIMS

[Claim(s)]

[Claim 1] The indicator electrode from which an oxidation reduction potential changes depending on the amount of residual chlorine contained into this liquid when a measuring object liquid is made to contact, It has the reference electrode in which constant potential is shown, without being dependent on the amount of residual chlorine contained into said liquid. In the residual chlorine measuring method which calculates the amount of residual chlorine contained into said measuring object liquid by measuring the electric amount which changes depending on the amount of residual chlorine contained into said measuring object liquid in the electrical circuit containing said indicator electrode and reference electrode It enables it to measure the electric amount corresponding to the current which prepares two indicator electrodes, the 1st and the 2nd, as said indicator electrode, impresses an electrical potential difference which is different from the outside, respectively between each of these 1st and 2nd indicator electrodes, and said reference electrode, and flows each circuit. It selects to the value of the field which comes to change depending on the amount of residual chlorine to which the flowing current contains one [this] circuit mainly into said measuring object liquid as magnitude of the applied voltage of one [said] circuit. And the circuit of this another side is selected as magnitude of the applied voltage of the circuit of said another side to the value of the field which becomes the current of the remainder depending on the content matter of the remainders other than the residual chlorine which the flowing current contains mainly into said measuring object liquid. The residual chlorine measuring method characterized by calculating the amount of residual chlorine contained into said measuring object liquid by calculating the value of the difference of the electric amount corresponding to the current which flows in said two circuits.

[Claim 2] The residual chlorine measuring method according to claim 1 characterized by preventing degradation of the ability to detect of said indicator electrode as it is made to change periodically the electrical potential difference impressed to said two circuits and the period which maintains the electrical potential difference suitable for removing the period which maintains the electrical potential difference of said measurement condition, and the oxide film produced on said two indicator-electrode front faces is established.

[Claim 3] It has the reference electrode in which constant potential is shown, without

being dependent on the amount of residual chlorine contained into the indicator electrode from which an oxidation reduction potential changes depending on the amount of residual chlorine contained into this liquid when a measuring object liquid is made to contact, and said liquid. In the quantitative analyzer of residual chlorine which calculates the amount of residual chlorine contained into said measuring object liquid by measuring the electric amount which changes depending on the amount of residual chlorine contained into said measuring object liquid in the electrical circuit containing said indicator electrode and reference electrode An electrical-potential-difference impression means to impress an electrical potential difference which prepares two indicator electrodes, the 1st and the 2nd, as said indicator electrode, and is different from the outside, respectively between each of these 1st and 2nd indicator electrodes, and said reference electrode, The quantitative analyzer of residual chlorine characterized by having a difference measurement means to measure the electric amount corresponding to the current which flows two circuits containing said the 1st and 2nd each and said reference electrodes of an indicator electrode, respectively, and a difference measurement means to search for the difference of the electric amount corresponding to the current which flows in said two circuits.

[Claim 4] The quantitative analyzer of residual chlorine according to claim 3 to which applied voltage of this electrical-potential-difference impression means is characterized by establishing the applied-voltage control means which controls said electrical-potential-difference impression means to have by turns two with the electrical potential differences suitable for removing the oxide film produced on the electrical potential difference of said measurement condition, and said two indicator-electrode front faces while applied voltage uses an adjustable thing as said electrical-potential-difference impression means.

[Claim 5] When changing to the electrical potential difference suitable for removing the oxide film which the applied voltage of said electrical-potential-difference impression means produced from the electrical potential difference of said measurement condition on said two indicator-electrode front faces, The signal from said difference measurement means at the time of the electrical potential difference of the measurement condition before the change being impressed is held. The quantitative analyzer of residual chlorine according to claim 4 characterized by establishing a hold means to maintain the HOLD status while maintaining the electrical potential difference suitable for removing the oxide film produced on the indicator-electrode front face said whose applied voltage is two.

[Claim 6] The amount detection probe of residual chlorine characterized by preparing

two indicator electrodes, the 1st and the 2nd, as said indicator electrode in the residual chlorine detection probe which has the indicator electrode from which an oxidation reduction potential changes depending on the amount of residual chlorine contained into this liquid when a measuring object liquid is made to contact, and the reference electrode in which constant potential is shown, without being dependent on the amount of residual chlorine contained into said liquid.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the quantitative analyzer of residual chlorine which measures the residual chlorine which is poured into the liquid of for example, tap water and others for disinfection etc., and remains into liquid.

[0002]

[Description of the Prior Art] For example, in purification plant, chlorine is poured into treated water for disinfection. Moreover, for example, in the industry of thermal power and nuclear electric power generation, a chemical processing plant, an iron manufacture, an ocean navigation fishing boat, etc., etc., prevention of the evil by propagation adhesion of the living thing to a channel etc. is benefited for impregnation of chlorine in the seawater used so much as cooling water or rinse water. In such a case, naturally the chlorine beyond the need does not remain to the wastewater after the tap water after processing, cooling, or washing. For example, residual chlorine concentration under wastewater returned to the sea after using it for cooling water is made desirable [that it is 0.02mg/l. or less] in order not to affect it to fish and shellfishes. For this reason, it is necessary to measure and monitor the residual chlorine of these service water continuously to accuracy.

[0003] By the way, when a platinum-electrode metallurgy electrode was used as an indicator electrode and silver/silver silver chloride electrode, a calomel electrode, or a copper electrode was conventionally used as a reference electrode as an approach of measuring underwater residual chlorine concentration, the electrical potential difference was changed and asked for the above-mentioned current by resistance which the current accompanying the oxidation reduction reaction produced on an indicator-electrode front face inserted in this electric closed circuit using the phenomenon of corresponding to the amount of residual chlorine. The most common residual chlorine detection equipment was only an electrical circuit which inserts the

comparatively small resistance for electrical-potential-difference conversion in the connection circuit of an indicator electrode and a reference electrode. By such method, for example, when reduction current is below 20microA extent, even if resistance of 1kohm was used for the potential difference between two electrodes, it was not set to 20mV or less, but will have measured the reduction current value in no electrical-potential-difference impressing. The common name of the current in such a cell configuration is carried out to the "GARUBANI (cell) current."

[0004] Moreover, from the former, in order to limit the measuring object matter, the PORARO method which impresses the electrical potential difference of less than 1 V extent higher than the potential of a reference electrode to an indicator electrode is also learned. That is, reduction current is produced when an electrical potential difference is positively impressed to inter-electrode from the outside. In this case, although the current to produce is called reduction PORARO current, the current value when changing applied voltage in this case changes with a natural thing, even if residual chlorine is this concentration. However, if it is made fixed applied voltage, since a PORARO current is proportional to residual chlorine concentration, the amount of residual chlorine can be calculated by measuring this PORARO current. Here, a monochrome lamin (NH2 Cl), dissolved oxygen, etc. which are raised with the semantics which influences the reduction current other than residual chlorine to this and the same rank are considered by the matter dissolved underwater. However, if the reduction PORARO current based on such dissolved matter does not set the electrical potential difference impressed to an electrode as a certain specific field, raw **** differs from its field range mutually. Therefore, even if it is test water with which the measuring object matter is limited, for example, a monochrome lamin (NH2 Cl), dissolved oxygen, etc. live together by setting this applied voltage as the specific range, it becomes possible to measure the content of only residual chlorine.

[0005]

[Problem(s) to be Solved by the Invention] by the way, the quality of an object called the "residual current" with the above conventional residual chlorine detection equipments even if there is no residual chlorine -- it is never unavoidable that an unknown oxidation reduction current arises. And since it will be placed between system of measurement by the surely quite complicated electrical circuit, generating of the "dark current" of the semi-conductor produced by it is never unavoidable. For this reason, in order to offset the "dark current" of the semi-conductor produced by adopting this residual current and complicated electrical circuit, the proofreading liquid containing residual chlorine decomposition reagents, such as a sodium

thiosulfate, was contacted to the indicator electrode, and the need had complicated actuation of aiming at electrical-zero proofreading. And since factors other than the above ideal conditions are included, the description which test water has is more complicated. Therefore, even if it leads the proofreading liquid of residual chlorine concentration zero prepared artificially, since there is no guarantee to which the residual-current value at that time becomes the same as the residual-current value in test water, such as seawater, it also has a possibility that an error may arise. That is, the residual current which should be offset as a blank value was a thing unrealizable with the conventional equipment using configuration liquid, although it became an ideal except residual chlorine to make it the numeric value acquired with test water with the same presentation.

[0006] This invention does not need complicated actuation of the calibration procedure which used proofreading liquid, does not have a possibility that the error which moreover originates in the residual current etc. may arise, and aims at offering the residual chlorine measuring method and equipment which can also measure the residual chlorine of ultralow volume to accuracy.

[0007]

[Means for Solving the Problem] In order to solve an above-mentioned technical problem, the residual chlorine measuring method concerning this invention (Configuration 1) The indicator electrode from which an oxidation reduction potential changes depending on the amount of residual chlorine contained into this liquid when a measuring object liquid is made to contact, It has the reference electrode in which constant potential is shown, without being dependent on the amount of residual chlorine contained into said liquid. In the residual chlorine measuring method which calculates the amount of residual chlorine contained into said measuring object liquid by measuring the electric amount which changes depending on the amount of residual chlorine contained into said measuring object liquid in the electrical circuit containing said indicator electrode and reference electrode It enables it to measure the electric amount corresponding to the current which prepares two indicator electrodes, the 1st and the 2nd, as said indicator electrode, impresses an electrical potential difference which is different from the outside, respectively between each of these 1st and 2nd indicator electrodes, and said reference electrode, and flows each circuit. It selects to the value of the field which comes to change depending on the amount of residual chlorine to which the flowing current contains one [this] circuit mainly into said measuring object liquid as magnitude of the applied voltage of one [said] circuit. And the circuit of this another side is selected as magnitude of the applied voltage of the

circuit of said another side to the value of the field which becomes the current of the remainder depending on the content matter of the remainders other than the residual chlorine which the flowing current contains mainly into said measuring object liquid. It considers as the configuration characterized by calculating the amount of residual chlorine contained into said measuring object liquid by calculating the value of the difference of the electric amount corresponding to the current which flows in said two circuits. As a mode of this configuration 1 (Configuration 2) The period which it is made to change periodically the electrical potential difference impressed to said two circuits, and maintains the electrical potential difference of said measurement condition, As the period which maintains the electrical potential difference suitable for removing the oxide film produced on said two indicator-electrode front faces is established, it considers as the configuration characterized by preventing degradation of the ability to detect of said indicator electrode.

[0008] Moreover, quantitative analyzer of residual chlorine concerning this invention (configuration 3) It has the reference electrode in which constant potential is shown, without being dependent on the amount of residual chlorine contained into the indicator electrode from which an oxidation reduction potential changes depending on the amount of residual chlorine contained into this liquid when a measuring object liquid is made to contact, and said liquid. In the quantitative analyzer of residual chlorine which calculates the amount of residual chlorine contained into said measuring object liquid by measuring the electric amount which changes depending on the amount of residual chlorine contained into said measuring object liquid in the electrical circuit containing said indicator electrode and reference electrode An electrical-potential-difference impression means to impress an electrical potential difference which prepares two indicator electrodes, the 1st and the 2nd, as said indicator electrode, and is different from the outside, respectively between each of these 1st and 2nd indicator electrodes, and said reference electrode, A difference measurement means to measure the electric amount corresponding to the current which flows two circuits containing said the 1st and 2nd each and said reference electrodes of an indicator electrode, respectively, It considers as the configuration characterized by having a difference measurement means to search for the difference of the electric amount corresponding to the current which flows in said two circuits, and is a mode of this configuration 3. (configuration 4) While applied voltage uses an adjustable thing as said electrical-potential-difference impression means It considers as the configuration characterized by establishing the applied-voltage control means by which the applied voltage of this electrical-potential-difference impression means

controls said electrical-potential-difference impression means to have by turns two with the electrical potential differences suitable for removing the oxide film produced on the electrical potential difference of said measurement condition, and said two indicator-electrode front faces. As a mode of this configuration 4 (Configuration 5) When changing to the electrical potential difference suitable for removing the oxide film which the applied voltage of said electrical-potential-difference impression means produced from the electrical potential difference of said measurement condition on said two indicator-electrode front faces, The signal from said difference measurement means at the time of the electrical potential difference of the measurement condition before the change being impressed was held, and while maintaining the electrical potential difference suitable for removing the oxide film produced on the indicator-electrode front face said whose applied voltage is two, it considered as the configuration characterized by establishing a hold means to maintain the HOLD status.

[0009] Furthermore, the residual chlorine detection probe concerning this invention (Configuration 6) The indicator electrode from which an oxidation reduction potential changes depending on the amount of residual chlorine contained into this liquid when a measuring object liquid is made to contact, In the residual chlorine detection probe which has the reference electrode in which constant potential is shown, without being dependent on the amount of residual chlorine contained into said liquid, it considers as the configuration characterized by preparing two indicator electrodes, the 1st and the 2nd, as said indicator electrode.

[0010]

[Embodiment of the Invention] The block diagram showing the configuration of the quantitative analyzer of residual chlorine which drawing 1 requires for one example of this invention, and drawing 2 are the residual chlorine detection probes concerning one example of this invention. Hereafter, a residual chlorine detection probe is explained to the residual chlorine measuring method and equipment list concerning one example, making drawing 1 and drawing 2 reference.

[0011] In drawing 1 , a sign 1 is a residual chlorine detection probe. This residual chlorine detection probe 1 has a reference electrode 11, the 1st indicator electrode 12, and the 2nd indicator electrode 13.

[0012] As for test water passage, the outline of the quantitative analyzer of residual chlorine of one example contacts test water to the residual chlorine detection probe 1 through 2. An electrical potential difference which is different in a list through the direct-current-voltage generating circuit 6 and the applied-voltage control circuit 5, respectively between a reference electrode 11 and the 2nd indicator electrode 13 is

impressed between a reference electrode 11 and the 1st indicator electrode 12. The current which flows in each circuit is transformed into an electrical potential difference through the detection resistance 3a and 3b, the difference of these electrical potential differences is searched for by the differential voltage amplification circuit 3, and the output is sent out outside through a status signal output circuit.

[0013] Reference electrodes 11 are silver/silver silver chloride electrode. This electrode is an electrode in which constant potential is shown, without being dependent on the amount of residual chlorine contained into the liquid contacted. The 1st indicator electrode 12 and the 2nd indicator electrode 13 are platinum electrodes. When contacting these indicator electrodes into a measuring object liquid, they are electrodes from which an oxidation reduction potential changes depending on the amount of residual chlorine contained into this liquid.

[0014] The direct-current-voltage generating circuit 6 generates required DC power supply from a source power supply, and is supplied to the applied-voltage control circuit 5. each from which the applied-voltage generating circuit 5 differs between a reference electrode 11 and the 2nd indicator electrode 13 in a list between a reference electrode and the 1st indicator-electrode electrode 12 -- while impressing an electrical potential difference, only predetermined time amount impresses periodically this applied voltage and the electrical potential difference which has reversed polarity. By this reverse voltage impression, dissolution clearance of the oxide film formed in each indicator-electrode front face is carried out, and sensibility lowering is prevented. That is, if reverse voltage is impressed, the current which flows inter-electrode becomes large, it will be returned by dissolved matter other than residual chlorine in an instant, and dissolution clearance of the oxide film by which it is said to an indicator-electrode front face that 1 atomic-layer extent formation is carried out will be carried out with it. Moreover, if applied voltage is returned to the usual condition, oxidation current will arise for several seconds and reduction current will decrease. In that case, the oxidation current which is reversed polarity may be shown depending on residual chlorine concentration. Reduction current increases in about 1 minute after voltage switching, and it reaches and stabilizes to equilibrium.

[0015] The applied-voltage control circuit 5 sends a command signal to the status signal output circuit 4 at the time of an applied-voltage change-over. In case it changes to reverse voltage, it controls to hold the signal sent to the status signal output circuit 4 from the differential voltage amplification circuit 3 at the event, and to send outside. The hold is canceled after changing and carrying out fixed time amount to the usual applied voltage from reverse voltage (after reduction current is stabilized).

Therefore, during impression of reverse voltage, the measured value in front of initiation of reverse voltage impression is held, and it is sent outside. In addition, the period of voltage switching can be carried out in about 2 minutes.

[0016] Usually, in the case of electrical-potential-difference impression, the electrical potential difference of 200-400mV is impressed to the 1st indicator electrode 12 (it impresses between reference electrodes 11), and an electrical potential difference higher about further 200-800mV than this is impressed to the 2nd indicator electrode 13. In this case, according to the 1st indicator electrode 12 with which the electrical potential difference of 200-400mV was impressed, although a reduction PORARO current changes depending on the content of free residual chlorine, the reduction PORARO current based on other dissolved matter, such as free residual chlorine, and a monochrome lamin (NH2 Cl) which differs in a reduction property, dissolved oxygen, is not produced. That is, the value corresponding to the amount of residual chlorine will be shown, without other dissolved matter other than free residual chlorine, such as a monochrome lamin and dissolved oxygen, containing temporarily the current produced through the 1st indicator electrode 12 in test water, and being influenced by these components also as a plate. however, the quality of an object called the "residual current" to this current -- an unknown oxidation reduction current and the "dark current" of an electrical circuit are included.

[0017] On the other hand, according to the 2nd indicator electrode 13 with which the electrical potential difference of 400-1200mV was impressed, the reduction PORARO current based on other dissolved matter, such as (it is not generated even if residual chlorine is high concentration called 20 mg/l), free residual chlorine, and a monochrome lamin (NH2 Cl) which differs in a reduction property, dissolved oxygen, is hardly produced not to mention the reduction PORARO current based on free residual chlorine not arising, either. That is, it can be said that the currents produced through the 2nd indicator electrode 13 are the "residual current" and the "dark current" mostly.

[0018] Therefore, it will be said that the difference of the current which flows the inside of the circuit containing the 1st indicator electrode 12, and the current which flows the inside of the circuit containing the 2nd indicator electrode 13 is physical quantity for which the "residual current" and the "dark current" are offset, and it depends on "the amount of residual chlorine." That is, the error factor by the residual current etc. is proofread and the output from the differential voltage amplification circuit 3 which amplifies the electrical potential difference produced in the detection resistance 3a and 3b, and takes the difference is a value corresponding to the amount

of residual chlorine in test water to accuracy. In addition, actually, since the "residual current" etc. changes according to applied voltage, it measures by performing zero adjustment by constituting so that each amplification factor can adjust the differential voltage amplification circuit 3 so that indicated value with no residual chlorine may become zero. Moreover, span proofreading is performed by the proofreading approaches, such as a colorimetric method, by also being able to adjust now actually the value of the detection resistance 3a and 3b, and adjusting these resistance.

[0019] Test water 24a introduced into the bead installation tub 22 with the test water installation tubing 24 is returned to the bead installation tub 22 with a part of bead 22a, and the test water passage 2 discharges it outside, after contacting delivery and the residual chlorine detection probe 1 to the measurement tub 21 with a part of detailed bead 22a which piles up in the bead installation tub 22. In this case, bead 22a carried to the measurement tub 21 with test water 24a repeats a collision on the front face of the 1st indicator electrode 12 and the 2nd indicator electrode 13, and always grinds the front face of these electrodes. Some polished beads are returned to the bead installation tub 22 with test water, and only test water is exported outside through a filter 23. The above-mentioned polish works in multiplication with an impression operation of above-mentioned reverse voltage, and brings epoch-making effectiveness to defecation of an electrode surface. When it actually tests, even if it does not carry out sensitivity settling at all over three months or more, it is checked that there are not an early condition and completely change.

[0020] The residual chlorine detection probe 1 fixes the indicator-electrode attaching part 15 to the point of the reference electrode maintenance rod 16 which carried out fitting immobilization in the approximately cylindrical probe base 17. The silver wire with which the front face oxidized is spirally coiled around the reference electrode maintenance rod 16, and the reference electrode 11 is constituted. As one [each] main front face faces outside, the 1st indicator electrode 12 and the 2nd indicator electrode 13 which consist of disc-like platinum set and arrange predetermined spacing in the indicator-electrode attaching part 15, and are being fixed to it. The lead wire of these indicator electrodes is further connected to an external circuit with the lead wire of a reference electrode 11 through the lead-wire takeoff connection 18 through the interior of a reference electrode indicator rod. Moreover, the reference electrode maintenance rod 16 is contained in the support cylinder 14. The end section is fixed to the probe base 17, and this support cylinder 14 is fixing the indicator-electrode attaching part 15 to the other end. Two or more minute dipping holes 14a and 14b etc. are formed in the lower part of the support cylinder 14, and air

hole 14c is prepared in the upper part. In addition, the interior of the indicator-electrode maintenance rod 16 is filled up with resin etc., and insulation of lead wire, prevention of **** and an open circuit, etc. are achieved.

[0021] This residual chlorine detection probe 1 can detect the reduction current produced between an indicator electrode and a reference electrode by making a reference electrode 11 contact through the dipping holes 14a and 14b etc. while contacting test water to two indicator electrodes 12 and 13.

[0022] Since structure with which an indicator electrode with the need of always giving [polish] a front face and defecating if possible, since detection sensitivity will be affected if a coat etc. be formed in a front face against a mechanical friction or an impact comparatively strongly [the reference electrode without the need of carrying out polish etc. comparatively weakly against a mechanical friction or an impact be contained in the directions cylinder 14, and it be protected, and] on the other hand be exposed outside be adopted, it be easy to process polishing etc.

[0023] According to one above-mentioned example, since he was trying to take the difference of the reduction current by two electrodes, the measured value against which the residual current etc. was set off could be obtained immediately, and the need of performing the complicated calibration procedure using proofreading liquid etc. was able to be abolished like before.

[0024] Moreover, since there is no possibility [like] of causing fluctuation to detection sensitivity etc. over a long period of time since the detailed bead was made mixing in test water and the electrode is always defecated while impressing reverse voltage to an electrode periodically, while always exact measurement is possible, it has an advantage, such as making a maintenance remarkably easy.

[0025]

[Effect of the Invention] As explained in full detail above, this invention prepares two indicator electrodes, the 1st and the 2nd, as an indicator electrode from which an oxidation reduction potential changes depending on the amount of residual chlorine contained into this liquid when a measuring object liquid is made to contact. By impressing an electrical potential difference different, respectively to the circuit containing each and the reference electrode of these 1st and 2nd indicator electrodes, detecting the PORARO current of each circuit, and taking the difference The complicated calibration procedure [residual current] using phase murder and proofreading liquid etc. is made unnecessary, and it enables it to perform exact measurement immediately.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the configuration of the quantitative analyzer of residual chlorine concerning one example of this invention.

[Drawing 2] It is drawing showing the configuration of the residual chlorine detection probe concerning one example of this invention.

[Description of Notations]

1 -- [-- A status signal output circuit, 5 / -- An applied-voltage control circuit, 6 / -- A direct-current-voltage generating circuit, 11 / -- A reference electrode, 12 / -- The 1st indicator electrode, 13 / -- The 2nd indicator electrode, 24a / -- Test water.] A residual chlorine detection probe, 2 -- Test water passage, 3 -- A differential voltage amplification circuit, 4

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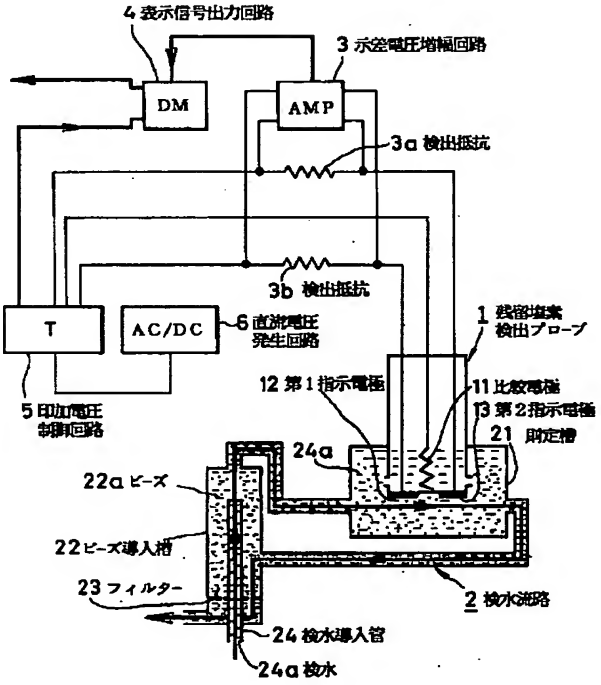
(54)【発明の名称】　残留塩素測定方法及び装置並びに残留塩素検出プローブ

(57)【要約】

【課題】　校正液を用いた校正操作等の繁雑な操作を必要とせず、しかも残余電流等に起因する誤差の生ずるおそれがなく、極微量の残留塩素をも正確に測定できる残留塩素測定方法及び装置を提供する。

【解決手段】　検水２４ａに接触させたときに検水に含有する残留塩素量に依存して酸化還元電位が変化する指示電極として第１及び第２の２つの指示電極１２，１３を設け、これら第１及び第２の指示電極のそれぞれと比較電極１１とを含む回路にそれぞれ異なる電圧を印加し、それぞれの回路のポーラロ電流を検知し、その差をとることによって、残余電流等を相殺し、校正液を用いた繁雑な校正操作等を不要にしてただちに正確な測定が行えるようにした。



【特許請求の範囲】
【請求項１】　測定対象液体に接触させたときに該液体に含有する残留塩素量に依存して酸化還元電位が変化する指示電極と、前記液体に含有する残留塩素量に依存せずに定電位を示す比較電極とを有し、前記指示電極と比較電極とを含む電気回路において前記測定対象液体に含有する残留塩素量に依存して変化する電気的量を測定することによって前記測定対象液体に含有する残留塩素量を求める残留塩素測定方法において、
前記指示電極として第１及び第２の２つの指示電極を設け、
これら第１及び第２の指示電極のそれぞれと前記比較電極との間に外部からそれぞれ異なる電圧を印加してそれぞれの回路を流れる電流に対応する電気的量を測定できるようにし、
前記一方の回路の印加電圧の大きさとして該一方の回路を流れる電流が主として前記測定対象液体に含有する残留塩素量に依存して変化するようになる領域の値に選定し、かつ、前記他方の回路の印加電圧の大きさとして該他方の回路を流れる電流が主として前記測定対象液体に含有する残留塩素以外の残余の含有物質に依存する残余の電流になる領域の値に選定し、
前記２つの回路に流れる電流に対応する電気的量の差の値を求めることにより前記測定対象液体に含有する残留塩素量を求めることを特徴とする残留塩素測定方法。
【請求項２】　前記２つの回路に印加する電圧を周期的に変化させるようにし、前記測定状態の電圧を維持する期間と、前記２つの指示電極表面に生じた酸化膜を除去するに適した電圧を維持する期間とを設けるようにして、前記指示電極の検出能力の劣化を防止するようにしたことを特徴とする請求項１に記載の残留塩素測定方法。
【請求項３】　測定対象液体に接触させたときに該液体に含有する残留塩素量に依存して酸化還元電位が変化する指示電極と前記液体に含有する残留塩素量に依存せずに定電位を示す比較電極とを有し、前記指示電極と比較電極とを含む電気回路において前記測定対象液体に含有する残留塩素量に依存して変化する電気的量を測定することによって前記測定対象液体に含有する残留塩素量を求める残留塩素測定装置において、
前記指示電極として第１及び第２の２つの指示電極を設け、
これら第１及び第２の指示電極のそれぞれと前記比較電極との間に外部からそれぞれ異なる電圧を印加する電圧印加手段と、
前記第１及び第２の指示電極のそれぞれと前記比較電極とを含む２つの回路を流れる電流に対応する電気的量をそれぞれ測定する差測定手段と、
前記２つの回路に流れる電流に対応する電気的量の差を求める差測定手段とを有することを特徴とする残留塩素測定装置。
【請求項４】　前記電圧印加手段として印加電圧が可変のものを用いると共に、該電圧印加手段の印加電圧が、前記測定状態の電圧と前記２つの指示電極表面に生じた酸化膜を除去するに適した電圧との２つを交互に有するように前記電圧印加手段を制御する印加電圧制御手段を設けたことを特徴とする請求項３に記載の残留塩素測定装置。
【請求項５】　前記電圧印加手段の印加電圧が、前記測定状態の電圧から前記２つの指示電極表面に生じた酸化膜を除去するに適した電圧に変化するとき、その変化前の測定状態の電圧が印加されている際の前記差測定手段からの信号をホールドし、前記印加電圧が２つの指示電極表面に生じた酸化膜を除去するに適した電圧を維持する間中そのホールド状態を維持するホールド手段を設けたことを特徴とする請求項４に記載の残留塩素測定装置。
【請求項６】　測定対象液体に接触させたときに該液体に含有する残留塩素量に依存して酸化還元電位が変化する指示電極と、前記液体に含有する残留塩素量に依存せずに定電位を示す比較電極とを有する残留塩素検出プローブにおいて、
前記指示電極として第１及び第２の２つの指示電極を設けたことを特徴とする残留塩素量検出プローブ。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、例えば水道水その他の液体に消毒等のために注入されて液中に残っている残留塩素を測定する残留塩素測定装置に関する。
【０００２】
【従来の技術】例えば、浄水場においては、消毒のために処理水に塩素が注入される。また、例えば、火力・原子力発電、化学プラント、製鉄や遠洋航海漁船などの産業において、冷却用水や洗浄用水として多量に用いられる海水等にも水路への生物の繁殖付着等による弊害の防止等のために塩素の注入がなされる。この様な場合、処理後の水道水や、冷却や洗浄後の排水に必要以上の塩素が残留するようなことがあってはならないことは当然である。例えば、冷却水に使用した後に海に戻される排水中の残留塩素濃度は、魚介類に対して影響を与えないためには０．０２ｍｇ／１以下であることが望ましいとされている。このため、これら用水の残留塩素を正確に測定して常時監視する必要がある。
【０００３】ところで、水中の残留塩素濃度を測定する方法として、従来は、白金電極や金電極を指示電極とし、銀／塩化銀電極や甘こう電極または銅電極を比較電極として用いた場合、指示電極表面上で生ずる酸化還元反応に伴う電流が残留塩素量に対応するという現象を利用して、この電気閉回路に挿入した抵抗によって上記電流を電圧に変換して求めていた。最も一般的な残留塩素

検出装置は、指示電極と比較電極の接続回路に電圧変換のための比較的小さな抵抗を挿入するだけの電気回路であった。このような方式では、例えば、還元電流が２０μＡ以下程度の場合は両電極間の電位差は、１ｋΩの抵抗を用いたとしても２０ｍＶ以下にしかならず、電圧無印加における還元電流値を測定していることになる。このような電池構成における電流を「ガルバニ（電池）電流」と俗称されている。

【０００４】また、従来から、測定対象物質を限定するために、比較電極の電位より高い１Ｖ以内程度の電圧を指示電極に印加するポーラロ方式も知られている。すなわち、電極間に外部から積極的に電圧を印加した場合においても還元電流は生ずる。この場合に生ずる電流を還元ポーラロ電流というが、この場合、印加電圧を変えたときの電流値は、残留塩素が同濃度であっても当然のことながら変わってくる。しかし、一定の印加電圧にしておけば、ポーラロ電流は残留塩素濃度に比例するので、このポーラロ電流を測定することによって残留塩素量を求めることができる。ここで、水中に溶存する物質には、残留塩素のほかに、還元電流を左右する意味ではこれと同列にあげられるモノクロラミン（ＮＨ2 Ｃｌ）や溶存酸素等も考えられる。しかし、これらの溶存物質に基づく還元ポーラロ電流は、電極に印加される電圧をある特定の領域に設定しないと生ぜず、その領域範囲が互いに異なる。したがって、この印加電圧を特定の範囲に設定することにより、測定対象物質を限定し、例えば、モノクロラミン（ＮＨ2 Ｃｌ）や溶存酸素等が共存する検水であっても、残留塩素のみの含有量を測定することが可能となる。

【０００５】

【発明が解決しようとする課題】ところで、上述のような従来の残留塩素検出装置では、残留塩素が皆無であっても、「残余電流」と呼ばれる対象物質不明の酸化還元電流が生ずることをどうしても避けることはできない。しかも、測定系にはどうしてもかなり複雑な電気回路が介在することになるので、それによって生じる半導体等の「暗電流」の発生をどうしても避けることができない。このため、この残余電流や複雑な電気回路を採用することで生じる半導体等の「暗電流」を相殺するため、チオ硫酸ナトリウム等の残留塩素分解試薬を含む校正液を指示電極に接触させて、電気的ゼロ校正を図る等の繁雑な操作が必要があった。しかも、検水が持つ性状は、上述のような理想的条件以外の要因を含むために、より複雑である。したがって、人為的に調製した残留塩素濃度ゼロの校正液を通じても、そのときの残余電流値が海水等の検水における残余電流値と同じになる保証はないので誤差が生ずるおそれもある。すなわち、ブランク値として相殺すべき残余電流は、残留塩素以外は同じ組成を持つ検水によって得た数値にすることが理想となるが、構成液を用いる従来の装置では実現できないものであった。

【０００６】本発明は、校正液を用いた校正操作等の繁雑な操作を必要とせず、しかも残余電流等に起因する誤差の生ずるおそれがなく、極微量の残留塩素をも正確に測定できる残留塩素測定方法及び装置を提供することを目的としたものである。

【０００７】

【課題を解決するための手段】上述の課題を解決するために、本発明にかかる残留塩素測定方法は、

（構成１）　測定対象液体に接触させたときに該液体に含有する残留塩素量に依存して酸化還元電位が変化する指示電極と、前記液体に含有する残留塩素量に依存せずに定電位を示す比較電極とを有し、前記指示電極と比較電極とを含む電気回路において前記測定対象液体に含有する残留塩素量に依存して変化する電気的量を測定することによって前記測定対象液体に含有する残留塩素量を求める残留塩素測定方法において、前記指示電極として第１及び第２の２つの指示電極を設け、これら第１及び第２の指示電極のそれぞれと前記比較電極との間に外部からそれぞれ異なる電圧を印加してそれぞれの回路を流れる電流に対応する電気的量を測定できるようにし、前記一方の回路の印加電圧の大きさとして該一方の回路を流れる電流が主として前記測定対象液体に含有する残留塩素量に依存して変化するようになる領域の値に選定し、かつ、前記他方の回路の印加電圧の大きさとして該他方の回路を流れる電流が主として前記測定対象液体に含有する残留塩素以外の残余の含有物質に依存する残余の電流になる領域の値に選定し、前記２つの回路に流れる電流に対応する電気的量の差の値を求めることにより前記測定対象液体に含有する残留塩素量を求めることを特徴とする構成とし、この構成１の態様として、

（構成２）　前記２つの回路に印加する電圧を周期的に変化させるようにし、前記測定状態の電圧を維持する期間と、前記２つの指示電極表面に生じた酸化膜等を除去するに適した電圧を維持する期間とを設けるようにして、前記指示電極の検出能力の劣化を防止するようにしたことを特徴とする構成としたものである。

【０００８】また、本発明にかかる残留塩素測定装置は、

（構成３）　測定対象液体に接触させたときに該液体に含有する残留塩素量に依存して酸化還元電位が変化する指示電極と前記液体に含有する残留塩素量に依存せずに定電位を示す比較電極とを有し、前記指示電極と比較電極とを含む電気回路において前記測定対象液体に含有する残留塩素量に依存して変化する電気的量を測定することによって前記測定対象液体に含有する残留塩素量を求める残留塩素測定装置において、前記指示電極として第１及び第２の２つの指示電極を設け、これら第１及び第２の指示電極のそれぞれと前記比較電極との間に外部からそれぞれ異なる電圧を印加する電圧印加手段と、前記

第１及び第２の指示電極のそれぞれと前記比較電極とを含む２つの回路を流れる電流に対応する電気的量をそれぞれ測定する差測定手段と、前記２つの回路に流れる電流に対応する電気的量の差を求める差測定手段とを有することを特徴とする構成とし、この構成３の態様として、

（構成４）　前記電圧印加手段として印加電圧が可変のものを用いると共に、該電圧印加手段の印加電圧が、前記測定状態の電圧と前記２つの指示電極表面に生じた酸化膜を除去するに適した電圧との２つを交互に有するように前記電圧印加手段を制御する印加電圧制御手段を設けたことを特徴とする構成とし、この構成４の態様として、

（構成５）　前記電圧印加手段の印加電圧が、前記測定状態の電圧から前記２つの指示電極表面に生じた酸化膜を除去するに適した電圧に変化するとき、その変化前の測定状態の電圧が印加されている際の前記差測定手段からの信号をホールドし、前記印加電圧が２つの指示電極表面に生じた酸化膜を除去するに適した電圧を維持する間中そのホールド状態を維持するホールド手段を設けたことを特徴とする構成とした。

【０００９】さらに、本発明にかかる残留塩素検出プローブは、

（構成６）　測定対象液体に接触させたときに該液体に含有する残留塩素量に依存して酸化還元電位が変化する指示電極と、前記液体に含有する残留塩素量に依存せずに定電位を示す比較電極とを有する残留塩素検出プローブにおいて、前記指示電極として第１及び第２の２つの指示電極を設けたことを特徴とする構成としたものである。

【００１０】

【発明の実施の形態】図１は本発明の一実施例にかかる残留塩素測定装置の構成を示すブロツク図、図２は本発明の一実施例にかかる残留塩素検出プローブである。以下、図１及び図２を参照にしながら、一実施例にかかる残留塩素測定方法及び装置並びに残留塩素検出プローブを説明する。

【００１１】図１において、符号１は残留塩素検出プローブである。この残留塩素検出プローブ１は、比較電極１１、第１指示電極１２及び第２指示電極１３を有する。

【００１２】一実施例の残留塩素測定装置の概略は、残留塩素検出プローブ１に検水流路を２を通じて検水を接触させ、比較電極１１と第１指示電極１２との間、並びに、比較電極１１と第２指示電極１３との間に直流電圧発生回路６及び印加電圧制御回路５を通じてそれぞれ異なる電圧を印加し、それぞれの回路に流れる電流を検出抵抗３ａ，３ｂを通じて電圧に変換し、これらの電圧の差を示差電圧増幅回路３によって求め、その出力を表示信号出力回路を通じて外部に送出するようにしたものである。

【００１３】比較電極１１は、銀／塩化銀電極である。この電極は接触される液体に含有する残留塩素量に依存せずに定電位を示す電極である。第１指示電極１２及び第２指示電極１３は、白金電極である。これら指示電極は、測定対象液体に接触させたときに該液体に含有される残留塩素量に依存して酸化還元電位が変化する電極である。

【００１４】直流電圧発生回路６は商用電源から必要な直流電源を発生させて印加電圧制御回路５に供給する。印加電圧発生回路５は、比較電極と第１指示電極電極１２との間、並びに、比較電極１１と第２指示電極１３との間に異なるそれぞれ電圧を印加するとともに、周期的にこの印加電圧と逆極性を有する電圧を所定の時間だけ印加する。この逆電圧印加により、各指示電極表面に形成される酸化膜を溶解除去して感度低下を防止する。すなわち、逆電圧を印加すると残留塩素以外の溶存物質によって電極間を流れる電流が大きくなって、指示電極表面に１原子層程度形成されるといわれる酸化膜は瞬時に還元されて溶解除去される。また、印加電圧を通常の状態に復帰させると、酸化電流が数秒間生じて還元電流は減少する。その場合、残留塩素濃度によっては逆極性である酸化電流を示すこともある。電圧切換え後１分程度で還元電流は増大し、平衡状態に達して安定化する。

【００１５】印加電圧制御回路５は、印加電圧切換時に表示信号出力回路４に指令信号を送る。逆電圧に切り替える際には、その時点で示差電圧増幅回路３から表示信号出力回路４に送られてきた信号をホールドして外部に送るように制御する。逆電圧から通常の印加電圧に切り替えて一定時間してから（還元電流が安定してから）そのホールドを解除する。したがって、逆電圧の印加中は、逆電圧印加の開始直前の測定値がホールドされて外部に送られる。なお、電圧切換えの周期は約２分程度にすることができる。

【００１６】通常電圧印加の際には、第１指示電極１２には２００～４００ｍＶの電圧が印加され（比較電極１１との間に印加）、第２指示電極１３にはこれよりもさらに２００～８００ｍＶ程度高い電圧が印加される。この場合、２００～４００ｍＶの電圧が印加された第１指示電極１２によれば、遊離残留塩素の含有量に依存して還元ポーラロ電流が変化するが、遊離残留塩素と還元特性を異にするモノクロラミン（ＮＨ2 Ｃｌ）や溶存酸素等の他の溶存物質に基づく還元ポーラロ電流は生じない。すなわち、第１指示電極１２を介して生ずる電流は、仮に検水中に遊離残留塩素のほかにモノクロラミンや溶存酸素等の他の溶存物質が含有されて板としても、これらの成分に左右されることなく残留塩素量に対応した値を示すことになる。ただし、この電流には「残余電流」と呼ばれる対象物質不明の酸化還元電流や電気回路の「暗電流」も含まれている。

【００１７】一方、４００～１２００ｍＶの電圧が印加された第２指示電極１３によれば、遊離残留塩素に基づく還元ポーラロ電流が生じないことは勿論のこと（残留塩素が２０ｍｇ／ｌという高濃度であっても生じない）、遊離残留塩素と還元特性を異にするモノクロラミン（ＮＨ２Ｃｌ）や溶存酸素等の他の溶存物質に基づく還元ポーラロ電流もほとんど生じない。すなわち、第２指示電極１３を介して生ずる電流は、ほぼ「残余電流」及び「暗電流」のみであるということができる。

【００１８】したがって、第１指示電極１２を含む回路中を流れる電流と、第２指示電極１３を含む回路中を流れる電流との差は、「残余電流」や「暗電流」が相殺されたものであって「残留塩素量」にのみ依存する物理量であるということになる。すなわち、検出抵抗３ａ，３ｂに生ずる電圧を増幅してその差をとる示差電圧増幅回路３からの出力は、残余電流等による誤差要因が校正されて正確に検水中の残留塩素量に対応した値である。なお、実際には、印加電圧に応じて「残余電流」等も変化するので、示差電圧増幅回路３をそれぞれの増幅率が調節できるように構成することによって、残留塩素が皆無の指示値がゼロになるようにゼロ調整を行って測定する。また、検出抵抗３ａ，３ｂの値も実際には調節できるようになっており、これらの抵抗値を調整することにより、比色法等の校正方法によってスパン校正を行うようになっている。

【００１９】検水流路２は、検水導入管２４によってビーズ導入槽２２に導入された検水２４ａを、ビーズ導入槽２２に滞留する微細なビーズ２２ａの一部とともに測定槽２１に送り、残留塩素検出プローブ１に接触させた後にビーズ導入槽２２にビーズ２２ａの一部とともに戻して外部に排出するものである。この場合、検水２４ａとともに測定槽２１に運ばれたビーズ２２ａは、第１指示電極１２及び第２指示電極１３の表面に衝突を繰り返してこれら電極の表面を常時研磨する。研磨したビーズの一部は検水と共にビーズ導入槽２２に戻され、検水だけがフィルター２３を通じて外部に移出される。上記研磨は上述の逆電圧の印加作用と相乗的に働いて電極表面の清浄化に画期的効果をもたらす。実際にテストしたところ、3か月以上に渡って感度調整を全くしなくても初期の状態と全く変化のないことが確認されている。

【００２０】残留塩素検出プローブ１は、略筒状のプローブ基部１７に嵌合固定した比較電極保持棒１６の先端部に指示電極保持部１５を固定したものである。比較電極保持棒１６には表面が酸化された銀線が螺旋状に巻かれて比較電極１１が構成されている。指示電極保持部１５には、円板状白金で構成される第１指示電極１２と第２指示電極１３とがそれぞれの一方の主表面が外部に面するようにして所定の間隔をおいて並べて固定されている。これら指示電極のリード線は比較電極指示棒の内部を通じ、さらにリード線取り出し部１８を通じて、比較電極１１のリード線と共に外部回路に接続されるようになっている。また、比較電極保持棒１６は支持筒１４内に収納されている。この支持筒１４はプローブ基部１７に一端部が固定され、他端部に指示電極保持部１５を固定している。支持筒１４の下部には複数の微小な通液孔１４ａ，１４ｂ等が設けられ、上部には通気孔１４ｃが設けられている。なお、指示電極保持棒１６の内部には樹脂等が充填されてリード線どうしの絶縁、侵液・断線の防止等が図られている。

【００２１】この残留塩素検出プローブ１は、検水を２つの指示電極１２，１３に接触させると共に、通液孔１４ａ，１４ｂ等を通じて比較電極１１にも接触させることによって、指示電極と比較電極との間に生ずる還元電流を検出することができるようになっている。

【００２２】比較的機械的摩擦や衝撃に弱くかつ研磨等をする必要のない比較電極は、指示筒１４内に収納されて保護され、一方、比較的機械的摩擦や衝撃に強くかつ表面に被膜等が形成されると検出感度に影響を与えるので可能であれば常時表面を研磨等施して清浄化しておく必要のある指示電極が外部に露出されるような構造を採用しているので、研摩等の処理を施しやすい。

【００２３】上述の一実施例によれば、２つの電極による還元電流の差をとるようにしているので、残余電流等が相殺された測定値をただちに得ることができ、従来のように、校正液等を用いた繁雑な校正操作を行う必要をなくすことができた。

【００２４】また、電極に周期的に逆電圧を印加すると共に、検水に微細なビーズを混入させて電極を常時清浄化しているので、長期間に渡って検出感度等に変動をきたすようなおそれがないので常に正確な測定が可能であるとともに、メンテナンスを著しく容易にする等の利点を有する。

【００２５】

【発明の効果】以上詳述したように、本発明は、測定対象液体に接触させたときに該液体に含有する残留塩素量に依存して酸化還元電位が変化する指示電極として第１及び第２の２つの指示電極を設け、これら第１及び第２の指示電極のそれぞれと比較電極とを含む回路にそれぞれ異なる電圧を印加し、それぞれの回路のポーラロ電流を検知し、その差をとることによって、残余電流等を相殺し、校正液を用いた繁雑な校正操作等を不要にしてただちに正確な測定が行えるようにしたものである。

【図面の簡単な説明】

【図１】　本発明の一実施例にかかる残留塩素測定装置の構成を示す図である。

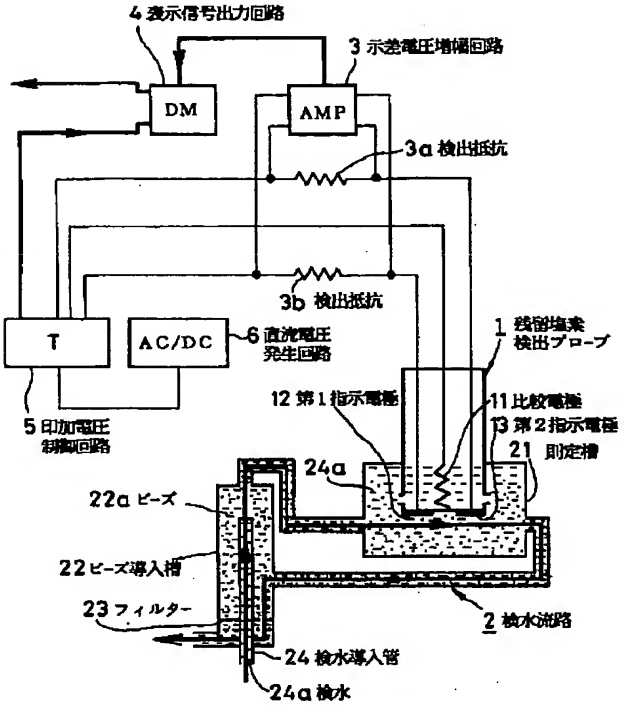
【図２】　本発明の一実施例にかかる残留塩素検出プローブの構成を示す図である。

【符号の説明】

１…残留塩素検出プローブ、２…検水流路、３…示差電圧増幅回路、４…表示信号出力回路、５…印加電圧制御

回路、６…直流電圧発生回路、１１…比較電極、１２…第１指示電極、１３…第２指示電極、２４ａ…検水。

【図１】



【図２】